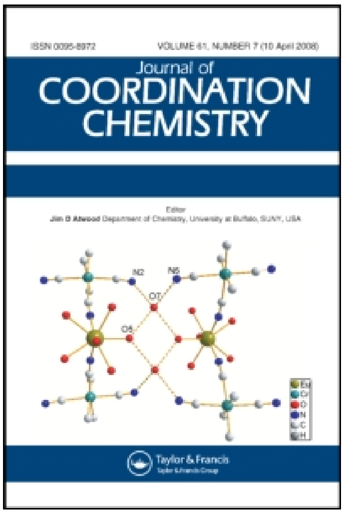

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Synthesis and spectroscopic studies of copper(II) complexes with 1-benzotriazol-1-yl-1-[(*p*-X-phenyl)hydrazono] propan-2-one

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Synthesis and spectroscopic studies of copper(II) complexes with 1-benzotriazol-1-yl-1-[(*p*-X-phenyl)hydrazono] propan-2-one

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A new series of copper(II) complexes resulted from the reaction of $CuCl_2 \cdot 2H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$ and 1-benzotriazol-1-yl-1-[(*p*-X-phenyl)hydrazono]-propan-2-one, X = H (HL^1), Cl (HL^2), Br (HL^3), OCH_3 (HL^4) and CH_3 (HL^5) have been synthesized and characterized by different spectral, magnetic measurements and elemental analysis. IR spectral data indicate that: (i) the free ligands exist in the hydrazo-ketone rather than azo-enol form in the solid state. Furthermore, the hydrazo-NH exists as hydrogen bonded to the keto-oxygen either as intra- or as intermolecular hydrogen bond. (ii) All ligands are neutral bidentate, coordinated to the copper(II) via hydrazone-nitrogen and the keto-oxygen atoms, and (iii) the ionic nature of ClO_4^- and coordinated and/or non-coordinated solvent molecules (H_2O or EtOH) with the possibility of hydrogen bonding with either the oxo-anions and/or triazole-nitrogen. The magnetic and spectral (UV/Vis and ESR) data indicate that these complexes have square planar, trigonal bipyramidal octahedral and tetrahedral structures. The nature of metal–ligand bonding is determined from the different electronic and ESR spectral parameters. The extent of distortion from ideal symmetry is also estimated and related to the electronic effects of the *p*-substituents, the nature of the ligand and counter ions.

Keywords: Benzotriazole derivatives; Copper(II); Complexes; Spectra

1. Introduction

Compounds containing triazole have attracted much interest because of their biological applications [1–4], exhibiting plant growth regulating activity [1]. Furthermore, triazoles appear frequently in the structures of various natural products and biologically active compounds [5]. Triazole-containing compounds appear in many metabolic products of fungi and primitive marine animals. Many triazoles having different functionalities are used as dyes and as photographic chemicals [6]. In addition, polymers derived from triazoles currently embody the most important practical

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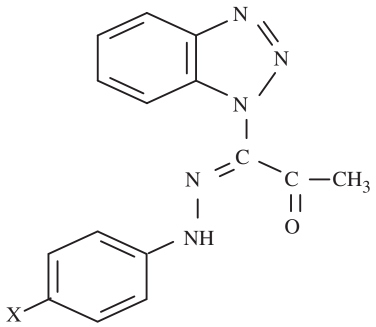


Figure 1. X = H (HL^1); Cl (HL^2); Br (HL^3); OCH_3 (HL^4); CH_3 (HL^5).

application of this heterocyclic system [3, 4]. The coordination chemistry of triazole and benzotriazole derivatives was studied due to their importance in industry and agriculture and their biological activity.

It is well known that the existence of a metal ion bonded to biologically active materials may enhance their activity by changing electronic and geometrical structures. Although Haasnoot and others have reviewed different metal complexes of triazole and benzotriazole as well as their derivatives [7], the ligating behaviors of 1-benzotriazo-1-yl-[(*p*-X-phenyl)hydrazono]propan-2-one, X = H, Cl, Br, OCH_3 or CH_3 are not reported in the literature. This study reports the synthesis and characterization of copper(II) complexes of the newly coordinating ligands, figure 1, which extends our previous investigations on hydrazones of heterocyclic nitrogen compounds [8–11].

2. Experimental

All chemicals were reagent grade quality obtained from BDH or Aldrich and used without further purification.

2.1. *Synthesis of the organic ligands*

The organic ligands were prepared according to the method given by Al-Awadi *et al.* [12, 13].

2.2. *Synthesis of Cu(II) complexes*

Copper(II) complexes were synthesized as follows: a hot ethanolic solution (30 cm^3) of copper(II) salt, $CuX_2 \cdot nH_2O$, X = Cl, or ClO_4, (0.001 or 0.002 mol) was added to a hot ethanolic solution (30–40 cm^3) of the corresponding ligand (0.0022 mol). The reaction mixture in each case was refluxed for 1–2 h, depending on the copper(II) salt and the ligand, with occasional stirring. The solid product in each case was filtered off while hot, washed several times with EtOH followed by Et_2O and dried in vacuum over P_4O_{10}. (Yield 60–70%.) The purity of the synthesized complexes was tested by TLC tests, melting points in most cases and elemental analyses, table 1.

Table 1. Elemental analysis [%found (%calculated)], color, melting point (°C) and molar conductivity data for the ligands and their Cu(II) complexes.

Compound	Color	m.p. ± 1°C	Λ_M[a]	$\mu_{eff.}$[b]	%C	%H	%N
HL^1	red	96			63.9(64.5)	4.6(4.7)	25.4(25.1)
HL^2	red	84			58.0(57.4)	4.2(3.8)	22.8(22.3)
HL^3	brown	82			50.7(50.3)	3.7(3.4)	19.9(19.6)
HL^4	yellow	85			62.6(62.1)	5.0(4.9)	22.9(22.7)
HL^5	red	87			65.1(65.5)	5.0(5.1)	23.5(23.9)
1. $[(HL^1)CuCl_2(H_2O)]$	green	195	86.92	2.12	42.4(41.7)	3.3(3.5)	16.3(16.2)
2. $[(HL^1)_2Cu]Cl_2 \cdot 2H_2O \cdot EtOH$	olive green	190	8.61	1.42	49.1(49.5)	4.3(4.6)	18.7(18.7)
3. $[(HL^1)_2Cu(H_2O)_2](ClO_4)_2$	yellowish green	> 300	155.92	1.82	43.6(43.8)	3.5(3.2)	17.3(17.1)
4. $[(HL^3)_2CuCl_2] \cdot 4H_2O$	brown	> 300	7.25	1.66	39.1(39.0)	3.1(3.5)	15.4(15.2)
5. $[(HL^4)_2CuCl_2]$	yellowish green	> 300	7.76	2.05	50.8(51.0)	4.2(3.9)	18.3(18.6)
6. $[(HL^2)CuCl_2] \cdot H_2O$	brown	205	3.86	1.97	38.7(38.6)	3.4(3.2)	14.8(15.0)
7. $[(HL^2)_2Cu](ClO_4)_2 \cdot EtOH$	brown	> 300	146.57	1.79	41.4(41.1)	3.4(3.2)	15.3(15.0)
8. $[(HL^2)_2Cu](ClO_4)_2 \cdot HL^2$	brown	217	151.23	1.98	44.9(44.9)	3.2(3.2)	17.1(17.5)
9. $[(HL^3)CuCl_2] \cdot EtOH$	brown	192	6.59	1.95	38.1(37.9)	3.3(3.3)	12.7(13.0)
10. $[(HL^5)_2Cu](ClO_4)_2 \cdot 3H_2O$	yellowish green	> 300	146.33	1.88	42.7(42.5)	3.8(4.0)	15.9(15.5)
11. $[(HL^3)_2Cu](ClO_4)_2 \cdot 2EtOH$	brown	> 300	146.44	2.01	38.1(38.1)	3.2(3.4)	12.9(13.1)
12. $[(HL^4)Cu(EtOH)](ClO_4)_2$	green	> 300	141.86	1.52	34.8(35.0)	3.2(3.4)	11.2(11.3)

[a] Molar conductivity values ($\Omega^{-1}\,cm^2\,mol^{-1}$).

[b] Room temperature effective magnetic moment per copper ion (B.M.).

2.3. *Physical measurements and analysis*

CHN analysis was obtained from LECO-CHNS 932 Analyzer at Analab, Kuwait University. FT-IR spectra were recorded as KBr discs with a Schimadzu 2000 FT-IR spectrophotometer. Electronic spectra were accomplished by a Carry Varian 5 UV/Vis/Nir spectrophotometer. The room temperature X-band ESR spectra were recorded for a polycrystalline and DMSO solutions in the presence of DPPH as a standard utilizing the ECS 106 ESR spectrometer. Room temperature magnetic susceptibility measurements for the complexes were determined by a Gouy balance using $Hg[Co(CN)_4]$ as the calibrant. Molar conductances of the complexes were measured for 1.00×10^{-3} DMSO solutions at room temperature using a Jenway 4020 conductivity meter.

3. Results and discussion

3.1. *General*

The reaction of the organic ligands with Cu(II) under reflux and different mole ratios gave the products presented in table 1. The formulation of these complexes is based on elemental analyses and electrical conductivity values, table 1. The molar conductivity values for freshly prepared DMSO solutions of the complexes indicated that all perchlorate containing complexes and complex **2** are 1 : 2 electrolytes while others are non-electrolytes [8–10]. The complexes are air stable, insoluble in most organic solvents and water but freely soluble in DMF, Py and DMSO. The complexes have higher melting points than their corresponding ligands indicating that they are thermally stable. This could be attributed to the formation of chelate rings and/or increased conjugation due to complexation.

Table 2. IR bands (cm^{-1}) with their tentative assignments for the ligands and their complexes.[a]

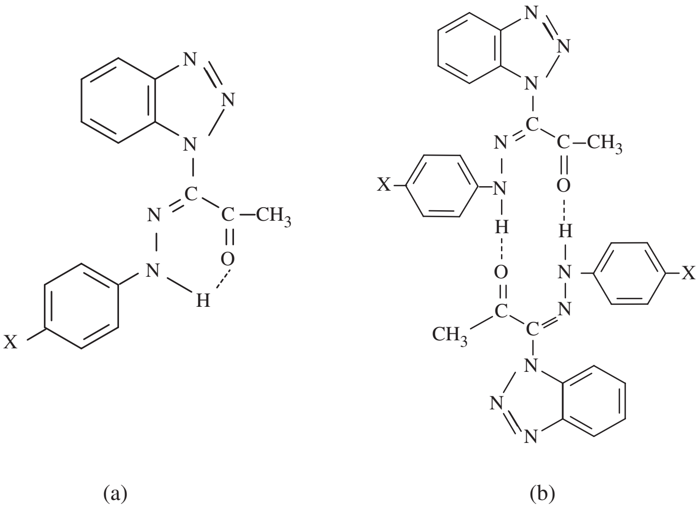
Compound	ν(NH) + H_2O[b]	ν(C=O)	ν(C=N)	ν(Cu–N)	ν(Cu–O)	ν(ClO_4)
HL^1	3270, 3400	1721vs	1600s			
HL^2	3220, 3400	1679vs	1602m			
HL^3	3245, 3418	1680s	1602s			
HL^4	3225, 3395	1650vs	1601s			
HL^5	3219, 3416	1674vs	1600m			
1. $[(HL^1)CuCl_2(H_2O)]$	3225, 3476	1736s	1574m	434w, 412w	531w	
2. $[(HL^1)_2Cu]Cl_2 \cdot 2H_2O \cdot EtOH$	3215, 3450, 3495	1674s	1577m	447w	500w	
3. $[(HL^1)_2Cu(H_2O)_2](ClO_4)_2$	3220, 3300	1733s	1588m	432w, 418w	500w	1095vs, 935m-w
4. $[(HL^3)_2CuCl_2] \cdot 4H_2O$	3286, 3422, 3572	1660m	1585m	432w	502w	
5. $[(HL^4)_2CuCl_2]$	3218	1648m-s	1578m	435w	512w	
6. $[(HL^2)CuCl_2] \cdot H_2O$	3246, 3370, 3572	1663s	1583m	428w	508w	
7. $[(HL^2)_2Cu](ClO_4)_2 \cdot EtOH$	3241, 3328, 3430	1661m-s	1586m	431w	509w	1093vs, 928m-w
8. $[(HL^2)_2Cu](ClO_4)_2 \cdot HL^2$	3308, 3400	1650s	1579m	420w	530w	1093vs, 950m-w
9. $[(HL^3)CuCl_2] \cdot EtOH$	3242, 3368, 3470	1637m	1584m	432w	503w	
10. $[(HL^5)_2Cu](ClO_4)_2 \cdot 3H_2O$	3220, 3438, 3407	1656s	1588m	433w	505w	1100vs, 930m-w
11. $[(HL^3)_2Cu](ClO_4)_2 \cdot 2EtOH$	3264, 3460	1660s	1578m-s	433w	505w	1118vs, 946m-w
12. $[(HL^4)Cu(EtOH)](ClO_4)_2$	3230, 3468	1629m-s	1580m	431w, 422w	504w	1107vs, 950m

[a] vs = very strong; s = strong; m = medium; m-s = medium-strong; w = weak.
[b] The bands ranged from broad medium to very strong.

3.2. *Infrared spectra*

The main IR spectral bands with their tentative assignments are given in table 2. The spectra of all ligands display a broad medium band in the 3220–3395 cm^{-1} range due to the different vibrational modes of –NH– of the hydrazo moiety. The broad band at 3400–3418 cm^{-1} could be taken as evidence for the involvement of the –NH– proton in the formation of hydrogen bonding of the –NH$\cdots$O– type [14, 15]. The bands at 3220–3395 cm^{-1} are not greatly affected by complex formation indicating the unchanged nature of the –NH– group in the complexes whereas the band at 3400–3418 cm^{-1}appeared with different position, intensity and shape. The triazole moiety displays a medium-strong band at 1554–1592 cm^{-1} in the spectrum of the free organic compounds. This band is not greatly affected by complex formation in most cases, indicating its non-bonding nature. All ligands display strong-medium bands at 1650–1677 and 1600–1602 cm^{-1} due to ν(C=O) and ν(C=N), respectively. The ν(C=O) values are in the order: $HL^1 > HL^2 \approx HL^3 > HL^5 > HL^4$ while the values due to ν(C=N) are *p*-substituent independent. Characteristic bands of –N=N– are not observed as supported from previous ^{1}H NMR studies [12, 13]. From the appearance of the ν(C=O) in the free ligands at a lower wavenumber relative to that of starting material, the dependence of its values on the nature of the *p*-substituents and the nearly unchanged values of the ν(C=N), the following conclusions can be drawn:

(a) the free ligands exist mainly in the keto-form in the solid state;
(b) there is no hydrazo-azo transformation or equilibrium;
(c) the presence of intramolecular or intermolecular hydrogen bonding of the type –NH$\cdots$O between the –NH– of the hydrazo-group (Brönsted acid) and the carbonyl-oxygen (Brönsted base), means that there may be a possibility of proton transfer between these two groups [16]. The presence of these types of hydrogen



(a) (b)

Figure 2. (a) Intramolecular and (b) intermolecular hydrogen bonding.

bonding indicates a number of structures in simultaneous equilibrium. Furthermore, the presence of proton donors and proton acceptors is prevalent in biological systems. Therefore, figure 2 could be assumed for the ligands in the solid state.

The bands due to ν(C=O) and ν(C=N) are shifted to lower wavenumbers in all complexes with changes in intensities indicating bonding to Cu(II). The appearance of new weak-medium bands at 418–490 and 500–531 cm^{-1} due to ν(Cu–N) and ν(Cu–O), respectively [16] can be taken as evidence for oxygen-nitrogen donor atoms in all ligands. Accordingly, the ligands act as neutral bidentate chelating agents coordinated to copper(II) via the azomethine–nitrogen and carbonyl–oxygen atoms forming the more stable five-membered chelate rings.

The spectra of all complexes, except **5**, display a broad medium band in the region of 3440–3490 cm^{-1} that could be attributed to the presence of solvent molecules (H_2O or EtOH). The nature of this band and its position may be taken as evidence for their participation in hydrogen bonding with the triazole moiety or with the oxyanions coordinated to copper(II) [16]. The IR spectra of ClO_4 containing complexes, table 2, indicate the ionic nature of the perchlorate [17]. The broad band at 3407–3572 cm^{-1} is attributed to hydrogen bonded H_2O or EtOH.

3.3. *Magnetic and spectral data*

Cu(II), like all transition metal ions, is capable of forming coordination compounds with a variety of ligands. The stereochemistry of Cu(II) complexes is dominated by the formation of non-regular structures involving significant bond length and bond angle distortions. The major responsibility for such behavior is the d^9-electron configuration and the Jahn-Teller effect. In the absence of X-ray crystallography, the correlation of the electronic and magnetic properties of the complexes to their structures is uncertain, especially if the ligands are polydentate [18]. Dimeric Cu(II) complexes can range from normal paramagnetic ($\mu_{\text{eff.}} = \mu_{\text{s.o.}}$) to ferromagnetic ($\mu_{\text{eff.}} > \mu_{\text{s.o.}}$ and $2J = 0\text{–}200\,\text{cm}^{-1}$) to antiferromagnetic but still paramagnetic ($\mu_{\text{eff.}} < \mu_{\text{s.o.}}$ and $2J = 0\text{–}200\,\text{cm}^{-1}$) to strongly antiferromagnetic ($2J > 300\,\text{cm}^{-1}$). For antiferromagnetic systems, monobridging chromospheres generally involve weak interactions, while dibridging systems are generally more strongly antiferromagnetic and in some cases diamagnetic [18].

The room temperature magnetic moment values for all complexes except $(\text{HL}^1)_2\text{CuCl}_2 \cdot 3\text{H}_2\text{O}$ (**2**) and $[(\text{HL}^4)\text{Cu(EtOH)}](\text{ClO}_4)_2$ (**12**), lie in the 1.88–2.12 B.M. range, table 1, indicating one unpaired electron as expected for magnetically dilute Cu(II) complexes. The higher magnetic moments than the spin-only value (1.73 B.M.) imply the presence of a low-laying excited term, which is able to mix its orbital angular momentum with the spin angular momentum of the ground state through orbital coupling [19]. This mixing is quite common for Cu(II) complexes with a distorted ligand field. The low symmetry components of the ligand also serve to split the ground state. The magnetic moment value of complex **2** is 1.42 B.M. This value indicates molecular association that could be achieved through a direct Cu–Cu interaction and/or magnetic exchange interaction through a bridging ligand(s). The bulkiness of the ligand and its nature ruled out direct Cu–Cu interaction; the observed value is probably due to magnetic exchange interaction through bridging ligand(s).

The electronic spectral data of the Cu(II) complexes as either nujol-mull or DMSO solution are given in table 3 and representative spectra are shown in figure 3. The spectrum of $[(\text{HL}^1)\text{CuCl}_2(\text{H}_2\text{O})]$, (**1**), figure 3(a), displays bands at 13 800, 11 600 and 10 600 cm^{-1} in case of nujol mull and only one band at 11 300 cm^{-1} as DMSO solution, figure 3(b).

These features are consistent with a Cu(II) in a trigonal bipyramidal or compressed octahedral ligand field [19]. The nature of the ligand, the IR spectra and elemental data confirm the presence of five coordinate Cu(II) complexes. Furthermore, the atom superposition and electron delocalization molecular orbital (ASED-MO) calculations for similar complexes [19] confirmed the trigonal-bipyramidal structure for $[(\text{HL}^1)\text{CuCl}_2(\text{H}_2\text{O})]$. Based on the MO calculations, there are four electronic transitions due to the trigonal-bipyramidal ligand field around the Cu(II). Out of these four transitions, only three are observed. The bands are assigned to d_{xz}, $\text{d}_{yz} \rightarrow \text{d}_{z^2}$ (13 800 cm^{-1}), $\text{d}_{xy} \rightarrow \text{d}_{z^2}$ (11 600 cm^{-1}) and $\text{d}_{x^2-y^2} \rightarrow \text{d}_{z^2}$ (10 600 cm^{-1}) transitions. The appearance of one broad band (11 300 cm^{-1}), the red shift and the shape change of the spectral features in DMSO are consistent with the change of the ligand field strength around the Cu(II) ion. This spectral band is consistent with either tetragonally distorted octahedral or trigonal bipyramidal ligand field around Cu(II). The ligand field change could be explained based on equations (1) and (2)

$$[(\text{HL}^1)\text{CuCl}_2(\text{H}_2\text{O})] + \text{DMSO} \rightarrow [(\text{HL}^1)\text{Cu(DMSO)}_4]\text{Cl}_2 \cdot \text{H}_2\text{O} \qquad (1)$$

$$\text{or} \quad [(\text{HL}^1)\text{CuCl}_2(\text{DMSO})] \cdot \text{H}_2\text{O} \qquad (2)$$

The room temperature X-band ESR spectrum of this complex, table 3 and figure 4(a), exhibits two g-values, $g_{\parallel} = 2.09$ and $g_{\perp} = 2.21$ characteristic of a $^2\text{A}'$ ground state in $\text{D}_{3\text{h}}$.

Table 3. Electronic and ESR spectral data for the Cu(II) complexes.

Compound	Medium	d-d transitions (cm^{-1})	$g_{\|\|}$	$g_{\perp}$	$g_{av.}$	G	$A_{\|\|}$ (G)	$g_{\|\|}/A_{\|\|}$ (cm)
1. $[(HL^1)CuCl_2(H_2O)]$	Solid	13 800, 11 600, 10 600,	2.09	2.21	2.17			
	DMSO	11 300	2.22	2.04	2.10			
2. $[(HL^1)_2Cu]Cl_2 \cdot 2H_2O \cdot EtOH$	Solid	12 400,	2.21	2.08	2.12			
	DMSO	16 300, 11 400						
3. $(HL^1)_2Cu(H_2O)_2](ClO_4)_2$	Solid	15 400, 12 400,	2.22	2.08	2.13	2.6		
	DMSO	12 500						
4. $[(HL^3)_2CuCl_2] \cdot 4H_2O$	Solid	15 350, 10 100,	2.32	2.07	2.15	4.5	112	207
	DMSO	12 500						
5. $[(HL^4)_2\ CuCl_2]$	Solid	15 200, 11 800, 12 500	2.24	2.06	2.12	4.2		
	DMSO	12 500						
6. $[(HL^2)CuCl_2] \cdot 2H_2O$	Solid	18 600, 14 500, 13 600, 10 500, 12 500(sh)	2.31	2.08	2.16	4.2	120	193
	DMSO	20 900, 16 700						
7. $[(HL^2)_2Cu](ClO_4)_2 \cdot EtOH$	Solid	18 600, 14 700, 13 500, 10 600, 12 300(sh)	2.35	2.06	2.16	5.5	131	180
	DMSO	19 800, 16 800						
8. $[(HL^2)_2Cu](ClO_4)_2 \cdot HL^2$	Solid	18 500, 14 700, 13 600, 10 500, 12 500(sh)	2.33	2.07	2.16	4.8	98	239
	DMSO	18 800, 16 700						
9. $[(HL^3)CuCl_2] \cdot EtOH$	Solid	18 550, 14 800, 13 500, 10 500, 12 400(sh)	2.26	2.08	2.14	3.2	129	175
	DMSO	20 900, 16 700						
10. $[(HL^5)_2Cu](ClO_4)_2 \cdot 3H_2O$[a]	Solid	18 600, 14 800, 13 600, 10 600, 12 500(sh)			2.14			
	DMSO	20 500, 16 800						
11. $[(HL^3)_2Cu](ClO_4)_2 \cdot 2EtOH$	Solid	20 100, 16 400,	2.24	2.05	2.11	4.8	185	121
	DMSO	22 300						
12. $[(HL^4)\ Cu](ClO_4)_2 \cdot EtOH$[b]	Solid	20 200, 16 300,	2.24	2.05	2.11	4.8	217	103
	DMSO	22 300						

[a] The value of $A_0 = 143$ G and $g_0 = 2.14$.
[b] This complex exhibits $\Delta M_s = \pm 2$ ($g = 4.13$) and a broad signal at 4715 G.

The deviation of the $g_{||}$ from the theoretical value (2.00) is attributed to the deviation from the ideal symmetry and/or the exchange coupling effects within the complexes in the solid state [20]. The obtained sharp lines are good evidence for the presence of exchange coupling between crystallographically equivalent sites.

The room temperature X-band ESR spectrum of complex **1** as DMSO solution displays two signals with $g_{||} = 2.22$ and $g_{-} = 2.04$, indicating the $d_{x^2-y^2}$ ground state in accord with the formation of a distorted octahedral ligand field around Cu(II) as a result of the interaction with DMSO. Furthermore, the ESR data confirm the formation of $[(HL^1)Cu(DMSO)_4]^{2+}$ in DMSO solution based on the electronic spectrum for this complex.

The nujol mull electronic spectrum of $(HL^1)_2CuCl_2 \cdot 3H_2O$ (EtOH), (**2**), figure 3c, displays only one band at 12 400 cm^{-1} characteristic of tetragonally distorted octahedral Cu(II) complexes. This band could be assigned as $^2B_{1g} \rightarrow ^2A_{2g}$ or $^2B_{1g} \rightarrow ^2B_{2g}$ transitions. The IR data of this complex showed that there is no coordinated water or coordinated EtOH molecules. These molecules (H_2O and EtOH) are present as water of hydration and EtOH solvation and/or involved in intramolecular hydrogen bonding. The IR spectra of the heated molecule (up to 130°C) did not show the characteristic band of ν(OH) of water or EtOH indicating desolvation. The reduced value of the magnetic moment ruled out the monomeric form. Therefore, six-coordination of the copper(II) could be achieved either by bridging triazole

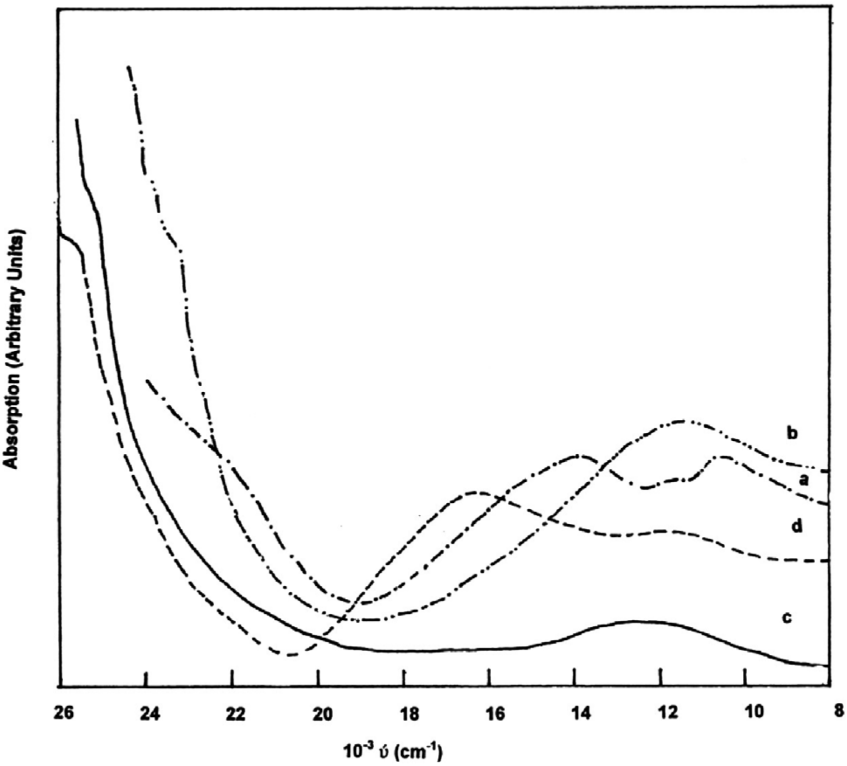


Figure 3. Electronic spectra of: (a) $[(HL^1)CuCl_2(H_2O)]$ as nujol mull; (b) $[(HL^1)CuCl_2(H_2O)]$ as DMSO solution; (c) $[(HL^1)_2Cu]Cl_2 \cdot 2(H_2O) \cdot EtOH$ as nujol mull; (d) $[(HL^1)_2Cu]Cl_2 \cdot 2(H_2O) \cdot EtOH$ as DMSO solution.

or through bridging Cl. The molar conductivity of this complex as DMSO solution indicates that it is a 1 : 2 electrolyte. Therefore, this complex may be formulated as $[(HL^1)_2Cu]Cl_2 \cdot 2H_2O \cdot (EtOH)$ or $[(HL^1)_2CuCl]Cl \cdot 2H_2O \cdot (EtOH)$. The latter formula may give $[(HL^1)_2Cu(DMSO)]Cl_2 \cdot 2H_2O \cdot (EtOH)$ in DMSO. Therefore, the structure in figure 5 is assumed.

The DMSO solution spectrum of the complex, figure 3(d), exhibits bands at 16 300 and 11 400 cm^{-1}. The ligand field around the Cu(II) indicates the interaction of DMSO molecules and/or the dissociation of the dimeric form followed by DMSO coordination. Furthermore, the spectral data are consistent with square pyramidal Cu(II) complexes. Therefore, bands are assigned to $^2B_1 \rightarrow ^2A_1$ (ν_1, 11 400 cm^{-1}) and $^2B_1 \rightarrow ^2B_2$ (ν_2, 16 300 cm^{-1}) transitions.

The room temperature X-band ESR spectrum of the polycrystalline sample, figure 4(b), displays axial type with $g_{\|} > g_{\perp}$, table 3. The spectral data confirm the $^2B_1$ ground state. The G value of 2.6 indicates the presence of copper centers in the solid state and the presence of a strong ligand field around the copper ions. Furthermore, the spectrum did not display any hyperfine lines in either the parallel or the perpendicular region. The spectrum displays a very weak signal at 1598 G ($g = 4.33$) which could be attributed to the forbidden $\Delta M_s = \pm 2$ transition, characteristic of the dimeric copper(II) complexes.

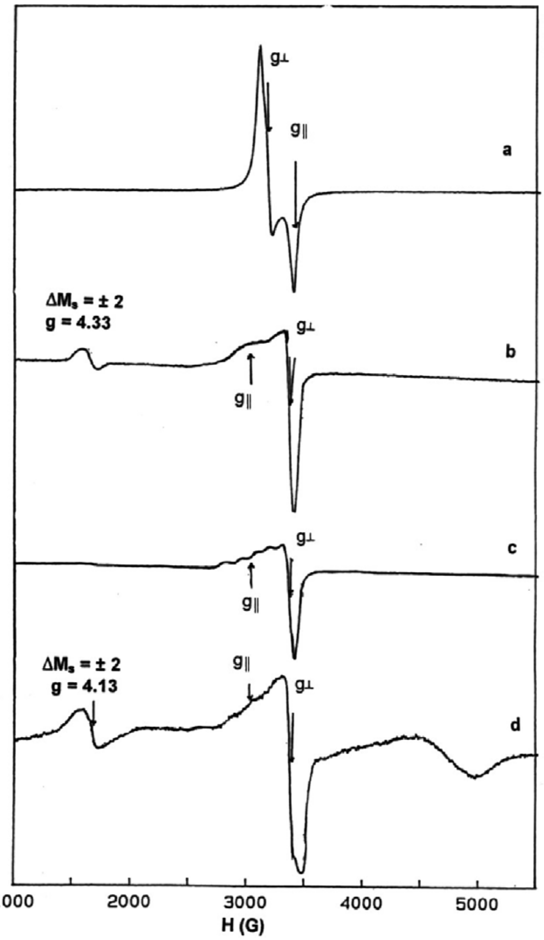


Figure 4. The room temperature X-band ESR spectra of: (a) $[(HL^1)CuCl_2(H_2O)]$; (b) $[(HL^1)_2Cu]Cl_2 \cdot 2(H_2O) \cdot EtOH$; (c) $[(HL^2)Cu](ClO_4)_2 \cdot HL^2$; (d) $[(HL^4)_2Cu](ClO_4)_2 \cdot EtOH$.

The electronic spectra of $[(HL^1)_2Cu(H_2O)_2](ClO_4)_2$ (**3**), $[(HL^3)_2CuCl_2] \cdot 4H_2O$ (**4**) and $[(HL^4)_2CuCl_2]$ (**5**) as nujol mulls, table 3, display a band in the range of $12\,400$–$10\,100\,cm^{-1}$ with a well-defined shoulder at $15\,200$–$15\,400\,cm^{-1}$. These spectral data are similar to those reported for tetragonally distorted octahedral Cu(II) complexes in D_4 or C_{4v} symmetry. In this symmetry there are three spin-allowed transitions in the visible and near IR regions due to $^2B_{1g}\rightarrow{}^2A_{2g}$, $^2B_{1g}\rightarrow{}^2B_{2g}$ and $^2B_{1g}\rightarrow{}^2E_g$ transitions in order of increasing energy. The energy level sequence depends on the amount of distortion due to the ligand field and the Jahn-Teller effects [21]. Accordingly, the main bands in the spectra are assigned to $^2B_{1g}\rightarrow{}^2E_g$ ($12\,400$–$10\,100\,cm^{-1}$) and $^2B_{1g}\rightarrow{}^2B_{2g}$ (15200–$15400\,cm^{-1}$) transitions, respectively, and the third band due to the $^2B_{1g}\rightarrow{}^2A_{2g}$ transition could not be observed perhaps due to its very low intensity and/or the distortion from ideal symmetry.

The spectra of these complexes as DMSO solution show only one asymmetric broad band at $12\,500\,cm^{-1}$ suggesting that all complexes have the same ligand field around

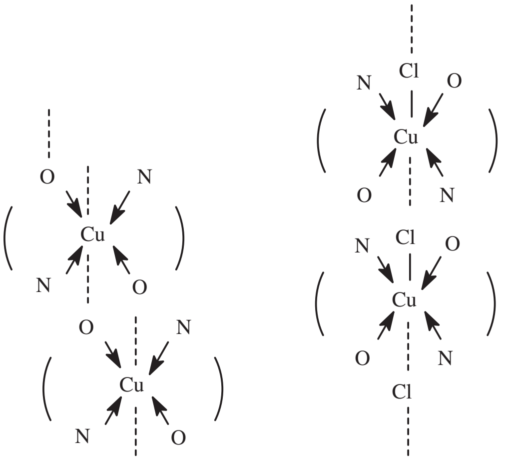


Figure 5. The assumed structure of the dimeric form of complex **2**.

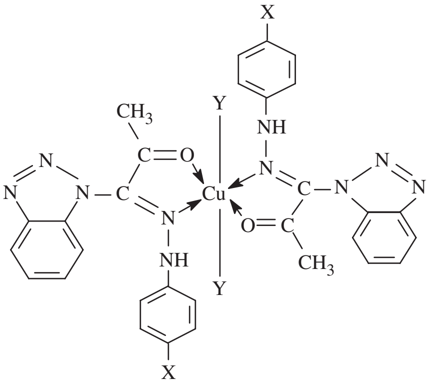
copper(II) in DMSO. The change in the band position relative to solid spectra indicates coordination of DMSO to the Cu(II), as shown in equation (3):

$$[(HL)_2CuCl_2]\cdot nH_2O \text{ or } [(HL)_2Cu(H_2O)_2](ClO_4)_2 + DMSO \rightarrow [(HL)_2Cu(DMSO)_2]^{2+} \quad (3)$$

The shape of the spectral band and its position are similar to the spectra of distorted octahedral Cu(II) complexes with a CuN_2O_4 chromophore [10, 11].

The X-band ESR spectra of the polycrystalline samples, table 3, are axial with two g-values, $g_{||} > g_{\perp}$. The $g_{||}$ for the HL^3 complex has the value of 2.32, whereas for the complexes of HL^1 and HL^4 have values of 2.22 and 2.24. Kivelson *et al.* pointed out that compounds having $g_{||} > 2.3$ are ionic compounds whereas those with $g_{||} < 2.3$ are covalent [21]. Therefore, the former complex is ionic whereas the latter two complexes are covalent. The ionic character of $[(HL^3)_2CuCl_2]\cdot 4H_2O$ is proved from the relative small value of $A_{||}$ of this complex (112 G). This complex showed deviation from planarity according to the quotient $g_{||}/A_{||} = 207$ cm. The $G = g_{||} - 2/g - 2$, measures the extent of exchange interaction between Cu(II) centers in the solid state. The values in table 3 indicate no significant interaction between copper centers for complexes containing HL^3 and HL^4 but a considerable interaction for the HL^1 complex. According to the spectral studies, molar conductivity and elemental analysis, figure 6, could be assumed for these complexes.

Representative nujol mull electronic spectra of complexes **6–10** are shown in figures 7(a) and (b) and the data are given in table 3. The spectra exhibit bands at 18 500–18 600, 14 700–14 800, 13 500–13 700 and 10 500–10 600 cm^{-1}. A weak shoulder at 12 300–12 500 cm^{-1} was observed in some cases. The energy of these bands does not exhibit any dependence on the nature of the substituents. The shapes, as well as band positions, are consistent with those reported for tetrahedral Cu(II) complexes [22]. Based on the crystal field and molecular calculations for copper(II) complexes with C_{2v} point groups, the band at 13 600–13 700 cm^{-1} is assigned to the $d_{xy} \rightarrow d_{xz}$



Y = Cl, DMSO or Cl

Figure 6. The assumed structure for complexes **3**–**5**.

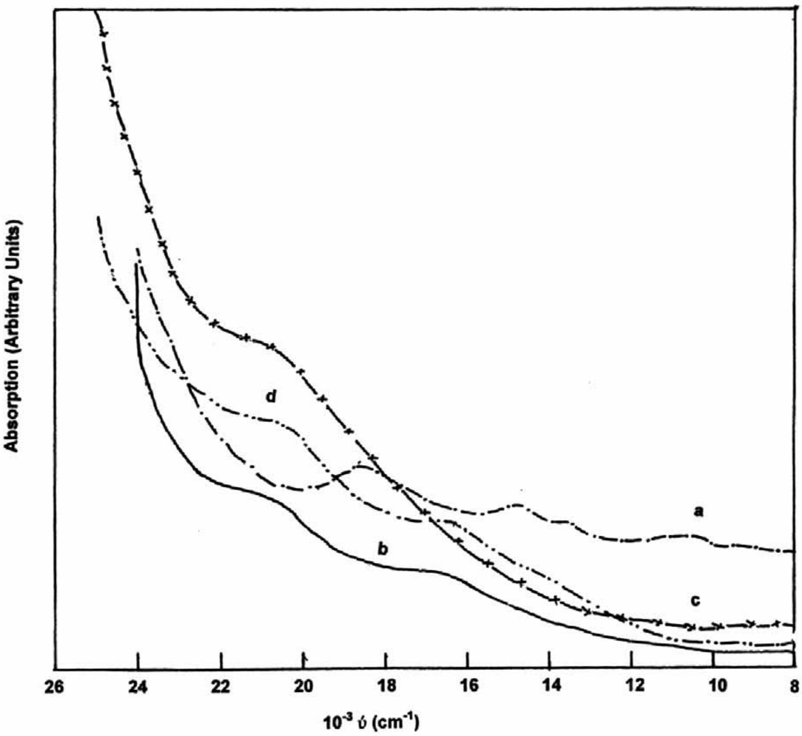


Figure 7. Electronic spectra of: (a) $[(HL^2)CuCl_2]\cdot H_2O$ as nujol mull; (b) $[(HL^2)CuCl_2]\cdot H_2O$ as DMSO solution; (c) $[(HL^2)_2Cu](ClO_4)_2\cdot 2EtOH$ as nujol mull; (d) $[(HL^2)_2Cu](ClO_4)_2\cdot 2EtOH$ as DMSO solution.

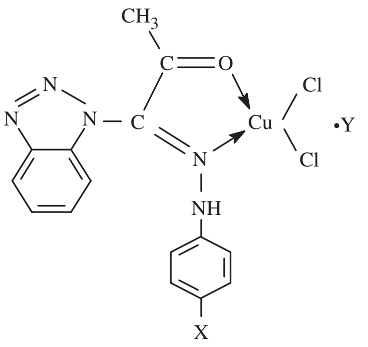
transition and that at 10 500–10 600 cm^{-1} to the $d_{yz}\rightarrow d_{xz}$ transition with the remaining transitions contributing to the overall band envelope.

The spectra of these complexes in DMSO exhibit bands at 20 900–19 800, 16 600–16 800 cm^{-1}, table 3. These spectral data are consistent with those reported for square-planar Cu(II) complexes. The higher energy band could be assigned as CT transitions. The broad band at 16 600–16 800 cm^{-1} is assigned to the $^2B_{1g} \rightarrow ^2E_g$ transition in D_{4h} symmetry. Other transitions in these spectra are not observed, perhaps due to the asymmetric nature of the observed band. This drastic change in the spectral shape and band positions indicates a change of the ligand field by either geometrical change and/or changing the coordinating donors through a substitution of the chloride ions by DMSO molecules followed by geometrical change from tetrahedral to square planar.

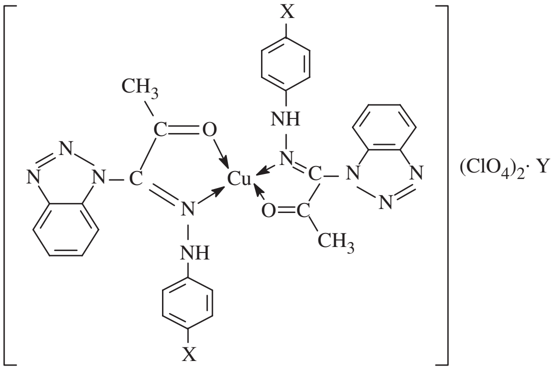
The X-band ESR spectra of these complexes at room temperature are axial with $g_{\parallel} > g_{\perp}$, except **10** which is isotropic, characteristic of $d_{x^2-y^2}$ ground state. A representative spectrum is shown in figure 4(c) and the data are given in table 3. Analysis of the spectra of **6**, **7** and **8** gave $g_{\parallel} = 2.31–2.35$, indicating the ionic nature of these complexes. Furthermore, the values of G-parameter, table 3, indicate a negligible exchange interaction between the copper centers in the solid state. The spectra of these three complexes display four hyperfine lines in the parallel regions ($A_{\parallel} = 98–131$ G) which is relatively small and characteristic of distorted tetrahedral Cu(II) complexes. The higher $g_{\parallel}$ and lower $A_{\parallel}$ values can be taken as evidence for the ionic nature of these complexes. The values of $A_{\parallel}$ are in the order of $[(HL^2)_2Cu](ClO_4)_2 \cdot HL^2$ (**8**) < $[(HL^2)CuCl_2] \cdot 2H_2O$ (**6**) < $[(HL^2)_2Cu](ClO_4)_2 \cdot EtOH$ (**7**). Furthermore the values of $g_{\parallel}/A_{\parallel} = 239–180$ cm are characteristic of the tetrahedral structure. Distortion from planarity to tetrahedral is therefore in the order $[(HL^2)_2Cu](ClO_4)_2 \cdot EtOH$ (**7**) < $[(HL^2)CuCl_2] \cdot 2H_2O$ (**6**) < $[(HL^2)_2Cu](ClO_4)_2 \cdot HL^2$ (**8**). The difference between complexes **7** and **8** is due to difference in the composition of the secondary sphere where EtOH is present in complex **7** and a molecule of ligand is present in complex **8**. Interaction between these molecules and the complex ion may be through van der Waals and/or intermolecular hydrogen bonding. The different spectral parameters of complex **9** could be attributed to the different ligand field around Cu(II). The spectrum of **10** exhibits isotropic shape with only $g_0 = 2.14$ and $A_0 = 143$ G, suggesting covalent nature. Therefore, figure 8 could be assumed for these complexes.

The nujol mull electronic spectra of complexes **11** and **12**, table 3, figures 7(c) and (d), display bands at 20 100–20 200 and 16 300–16 400 cm^{-1}, characteristic of square planar Cu(II) complexes. These spectral features are assigned to $^2B_{1g} \rightarrow ^2E_g$ (ΔE_{xz}) and $^2B_{1g} \rightarrow 2B_{2g}$ (ΔE_{xy}) transitions, respectively. Based on the elemental analysis, molar conductivity, IR and electronic spectral data a dimeric square-planar structure for complex **12**, figure 9, could be assumed. The dimeric form was proved from the reduced magnetic moment value of 1.52 B.M. The spectra of the two complexes in DMSO display only one band at 20 100–21 000 cm^{-1}. No bands are located in the lower energy side of the visible region. Such spectral features are characteristic of many Cu(II) complexes in a square-planar ligand field. DMSO is not coordinated to complex **11** but may solvate it. The dimeric Cu(II) complex **12** may be dissociated into a monomeric form with stoichiometric structure $[(HL^4)2Cu](ClO_4)_2$ or $[(HL)Cu(DMSO)_2](ClO_4)_2$. Attempts to isolate the solid products failed.

The room temperature X-band ESR spectra of **11** and **12** are recorded. A representative spectrum is shown in figure 4(d) and the data are collected in table 3. The spectra display two g-values. In both cases the $g_{\parallel} > g_{\perp}$ suggesting $d_{x^2-y^2}$ ground state, rather similar to the spectra reported for square-planar Cu(II) complexes [23, 24]. The spectra of the two complexes show a hyperfine structure with four components corresponding to the interaction of the unpaired electron with the nuclear spins of ^{63}Cu and ^{65}Cu both



Y = H_2O (**6**), EtOH (**9**)



Y = EtOH (**7**), HL (**8**), H_2O (**10**)

Figure 8. The assumed structures for the complexes **6**–**10**.

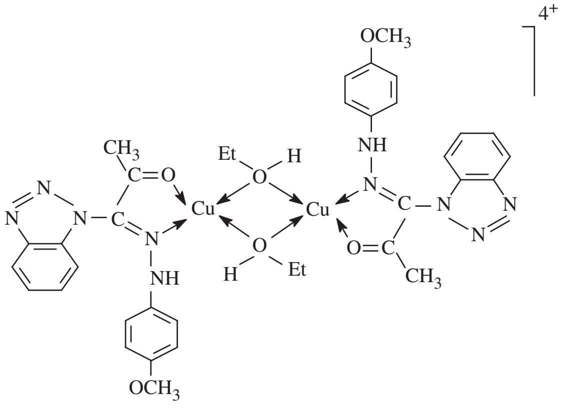


Figure 9. The assumed structure for compound **12**.

of which have $I = 3/2$. The values of $G = 4.8$ for **11** and **12**, indicate negligible exchange interaction between the Cu(II) centers in the solid. Furthermore, these values indicate moderate ligand field strength around the Cu(II) and are comparable to those obtained for square-planar Cu(II) complexes with CuN_2O_2 chromophore.

The values of $g_{\parallel}$ (2.24 for complexes **11** and **12**) and $A_{\parallel}$ (185 and 217 G, respectively), table 3, are consistent with the covalent character of these complexes. The $g_{\parallel}/A_{\parallel}$ values of 121 and 103 cm for **11** and **12**, respectively, indicate that the complexes are in the range reported for square-planar complexes (105 to 135 cm). Furthermore, these values indicate that complex **12** is more planar than complex **11**. The planarity of **12** relative to **11** may be attributed to the dimeric nature and the lack of steric effects around Cu(II), where only one ligand molecule is bonded to the Cu(II), while in compound **11** there are two bulky ligands around Cu(II).

The spectra of complex **12** show a weak signal at the half field region 1676 G ($g = 4.13$) due to the forbidden $\Delta M_s = \pm 2$ transition in the dimeric copper complex. The spectra also show a weak broad signal at the high field region at 4715 G (Δ peak to peak = 415 G). The latter signal is assigned to perpendicular and parallel components of the singlet ($S' = 0$, $M_s = 0$) to triplet ($S' = 1$, $M_s = 1$) transitions. Furthermore the appearance of the $\Delta M_s = \pm 2$ transition could be taken as evidence that the Cu–Cu separation lies between 3–5 Å. The intensity of this signal decreases and disappears as the separation distance increases [25, 26].

In D_{4h} symmetry, Cu(II) complexes with ${}^2B_{1g}$ ground state, the parallel ($k_{\parallel}$) and perpendicular ($k_{\perp}$) components of the orbital reduction factor k, which are the measure of the covalency, could be calculated from the relations [27]:

$$k_{\parallel}^2 = (g_{\parallel} - 2.0023)\Delta E_{xy}/8\lambda_0$$

$$k_{\perp}^2 = (g_{\perp} - 2.0023)\Delta E_{xz}/2\lambda_0$$

$$k^2 = 1/3(k_{\parallel}^2 + 2k_{\perp}^2)$$

where λ_0 is the spin orbit coupling constant for free Cu(II) and ΔE_{xy} and ΔE_{xz} are the electron transition energies. The calculated values of $k_{\parallel}^2$ and $k_{\perp}^2$ for complex **11**, are 0.59 and 0.70 while for complex **12**, the values are 0.58 and 0.71, respectively, from which $k_{\parallel}$ and $k_{\perp} = 0.67$ and 0.36 for both complexes are calculated. The value of $k = 0.82$, lower than unity, indicates the covalent character of these two complexes.

The in-plane σ-covalency parameter α^2 (Cu) was calculated following Kivelson and Neiman's simplified expression [28]:

$$\alpha^2(\text{Cu}) = A_{\parallel}/0.036 + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

The calculated values 0.82 and 0.86 for complexes **11** and **12**, respectively, are comparable to those for great covalency in the metal–ligand bonding.

4. Conclusion

The interaction of the new chelating agents 1-benzotriazol-1yl-1-[(*p*-X-phenylhydrazone]-propan-2-one (HL^{1-5}) with Cu(II) salts gave Cu(II) complexes with different stoichiometry, stereochemistry, spectral and magnetic properties depending on the electronic and bulkiness effects of the *p*-substituents. In all complexes the ligands are neutral bidentate coordinated to Cu(II) via the carbonyl–oxygen and hydrazone-nitrogen. The triazole nitrogen atoms are hydrogen bonded to the molecule of solvation

(H_2O or EtOH). The isolated complexes are classified into: (i) trigonal bipyramidal complexes **1**; (ii) tetragonally distorted Cu(II) complexes **2** (dimer), **3**–**5**; (iii) tetrahedral copper(II) complexes **6**–**10** and (iv) square planar complexes **11** and **12**. The ESR and electronic spectral data indicate the intermediate ligand field strength for these classes of ligands. Furthermore, the nature of metal-ligand bonding in the complexes of HL^1, HL^4, HL^5 is covalent, while the complexes of HL^2 and HL^3 are ionic. This is due to the different electronic effects of the *p*-substituents.

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